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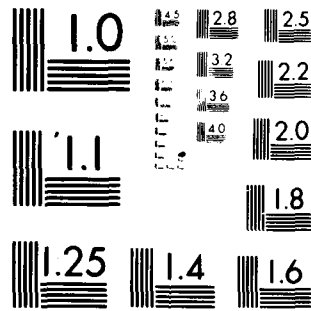
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L';  $[S]-L_3Ru_3(CO)_9$ , suspended in isooctane, yields  $[S]-LRu(CO)_4$  when irradiated at 436 nm under 1 atm CO. In the presence of 0.05 M  $L' = P(OCH_2)_3CCH_2CH_3$  436 nm irradiation of the  $[S]-L_3Ru_3(CO)_9$  yields  $[S]-LRu(CO)_3L'$ , but 0.05 M  $L' = PPh_3$  does not yield  $[S]-LRu(CO)_3L'$ , in contrast to the solution species  $[(EtO)_3SiCH_2CH_2PPh_2]_3Ru_3(CO)_9$  that gives  $[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_3L'$  for  $L' = CO, PPh_3$ , or  $P(OCH_2)_3CCH_2CH_3$  upon 436 nm irradiation. The  $[S]-LRu(CO)_4$  formed photochemically from  $[S]-L_3Ru_3(CO)_9$  undergoes 355 nm photoreaction to regenerate  $[S]-L_3Ru_3(CO)_9$  when isooctane solutions are purged with  $N_2$  to remove CO. The  $[S]-LRu(CO)_4$  formed by reacting  $SiO_2$  with  $[(EtO)_3SiCH_2CH_2PPh_3]Ru(CO)_4$  yields loss of all metal carbonyls from the surface and no detectable  $[S]-L_3Ru_3(CO)_9$  under an  $N_2$  purge. In no case are metal carbonyl species photochemically released into solution; the Ru-P bond is photoinert. The photochemical disassembly-reassembly of  $[S]-L_3Ru_3(CO)_9$  establishes that (1) the  $-Ru(CO)_4$  centers formed photochemically are immobile, remaining close enough to reform the original cluster by photochemical extrusion of CO; (2) each Ru of the  $Ru_3$  clusters is anchored to the surface, otherwise recovery of  $[S]-L_3Ru_3(CO)_9$  would be poor; and (3)  $-Ru(CO)_4$  centers on  $[S]-LRu(CO)_4$  formed from  $[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_4$  are sufficiently isolated to prevent cluster formation and thus the photogenerated 16-valence-electron  $[S]-LRu(CO)_3$  species are isolated from each other at dilute coverages.

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"PHOTOCHEMISTRY OF SURFACE-CONFINED MONONUCLEAR AND TRINUCLEAR RUTHENIUM  
CARBONYL COMPLEXES. DIRECT EVIDENCE FOR THE ABILITY TO ISOLATE  
PHOTOGENERATED INTERMEDIATES FROM EACH OTHER ON HIGH SURFACE AREA SILICA"

by

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Prepared for publication in the Journal of the American Chemical Society

January 4, 1982

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Photochemistry of Surface-Confined Mononuclear and Trinuclear Ruthenium Carbonyl Complexes. Direct Evidence for the Ability to Isolate Photogenerated Intermediates from Each Other on High Surface Area Silica

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Abstract:

Functionalized high surface area ( $400 \text{ m}^2/\text{g}$ )  $\text{SiO}_2$ ,  $[\text{S}]-\text{LRu}(\text{CO})_4$  and  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$ , has been synthesized by reacting  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]\text{Ru}(\text{CO})_4$  or  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]_3\text{Ru}_3(\text{CO})_9$  with  $\text{SiO}_2$ . The photoexcitation of  $[\text{S}]-\text{LRu}(\text{CO})_4$  and  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  at a coverage of  $\sim 3 \times 10^{-11} \text{ mol}/\text{cm}^2$  of  $-\text{Ru}(\text{CO})_4$  or  $-\text{Ru}_3(\text{CO})_9$  yields dissociative loss of CO from the mononuclear centers or metal-metal bond cleavage for the trinuclear species as judged from the photoproducts formed:  $[\text{S}]-\text{LRu}(\text{CO})_4$  under  $355 \text{ nm} \pm 20 \text{ nm}$  irradiation yields  $[\text{S}]-\text{LRu}(\text{CO})_3\text{L}'$  ( $\text{L}' = {}^{13}\text{CO}, \text{PPh}_3, \text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ ) when suspended in isooctane solution containing  $0.05 \text{ M L}'$ ;  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$ , suspended in isooctane, yields  $[\text{S}]-\text{LRu}(\text{CO})_4$  when irradiated at  $436 \text{ nm}$  under  $1 \text{ atm CO}$ . In the presence of  $0.05 \text{ M L}' = \text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$   $436 \text{ nm}$  irradiation of the  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  yields  $[\text{S}]-\text{LRu}(\text{CO})_3\text{L}'$ , but  $0.05 \text{ M L}' = \text{PPh}_3$  does not yield  $[\text{S}]-\text{LRu}(\text{CO})_3\text{L}'$ , in contrast to the solution species  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]_3\text{Ru}_3(\text{CO})_9$  that gives  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]\text{Ru}(\text{CO})_3\text{L}'$  for  $\text{L}' = \text{CO}, \text{PPh}_3$ , or  $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$  upon  $436 \text{ nm}$  irradiation. The  $[\text{S}]-\text{LRu}(\text{CO})_4$  formed photochemically from  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  undergoes  $355 \text{ nm}$  photoreaction to regenerate  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  when isooctane solutions are purged with  $\text{N}_2$  to remove CO. The  $[\text{S}]-\text{LRu}(\text{CO})_4$  formed by reacting  $\text{SiO}_2$  with  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]\text{Ru}(\text{CO})_4$  yields loss of all metal carbonyls from the surface and no detectable  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  under an  $\text{N}_2$  purge. In no case are metal carbonyl species photochemically released into solution; the Ru-P bond is photoinert. The photochemical disassembly-reassembly of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  establishes that (1) the  $-\text{Ru}(\text{CO})_4$  centers formed photochemically are immobile, remaining close enough to reform the original cluster by photochemical extrusion of CO; (2) each Ru of the  $\text{Ru}_3$  clusters is anchored to the surface, otherwise recovery of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  would be poor; and (3)  $-\text{Ru}(\text{CO})_4$  centers on  $[\text{S}]-\text{LRu}(\text{CO})_4$  formed from  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]\text{Ru}(\text{CO})_4$  are sufficiently isolated to prevent cluster formation and thus the photogenerated 16-valence-electron  $[\text{S}]-\text{LRu}(\text{CO})_3$  species are isolated from each other at dilute coverages.

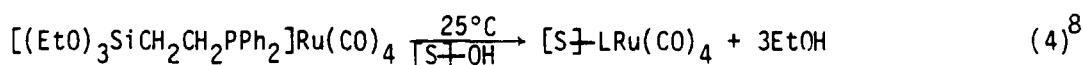
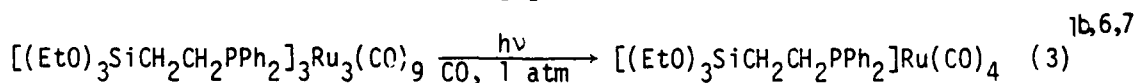
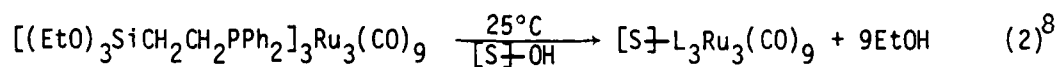
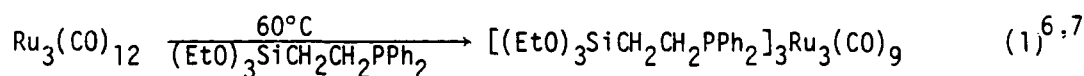
Photochemistry of Surface-Confined Mononuclear and Trinuclear Ruthenium Carbonyl Complexes. Direct Evidence for the Ability to Isolate Photogenerated Intermediates from Each Other on High Surface Area Silica

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Photoactivation of homogeneous organometallic catalysts by light-induced extrusion of 2-electron donor ligands or metal-metal bond cleavage has been demonstrated.<sup>1-5</sup> A problem that has arisen is that the reactive solution species can recombine with the extruded ligand or can react with each other to form inactive clusters.<sup>1</sup> We now report the synthesis and photochemical behavior of  $\text{LRu}(\text{CO})_4$  and  $\text{L}_3\text{Ru}_3(\text{CO})_9$  confined to the surface of high surface area silica. The results illustrate that immobilization of precursors to coordinatively unsaturated species prevents cluster formation, when the surface coverage is sufficiently low. Further, photodeclusterification of anchored  $\text{L}_3\text{Ru}_3(\text{CO})_9$  is reversible due to the immobilization of the fragments.

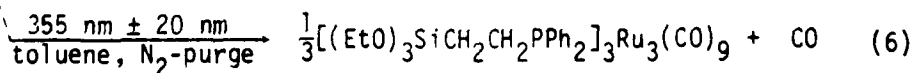
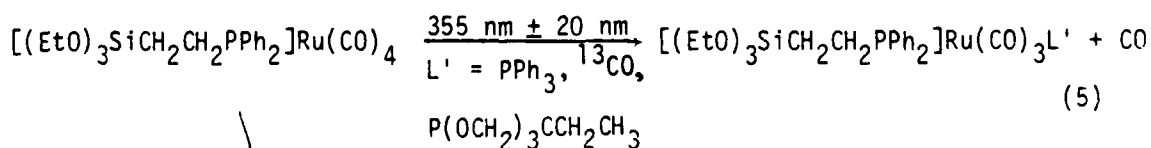
Equations (1)-(4), each having precedence in the literature,<sup>1b,6-8</sup> outline



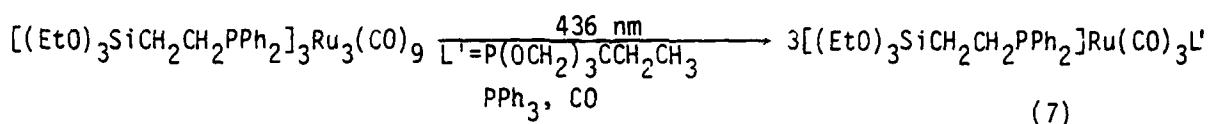
the procedure used to anchor  $\text{LRu}(\text{CO})_4$  and  $\text{L}_3\text{Ru}_3(\text{CO})_9$  to the surface of high surface area,  $400 \text{ m}^2/\text{g}$ ,  $\text{SiO}_2$  (Alfa).<sup>9</sup> The key to the preparation of the surface-confined  $\text{LRu}(\text{CO})_4$  and  $\text{L}_3\text{Ru}_3(\text{CO})_9$  is to use the phosphine ligand

(EtO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (Strem) to prepare the derivatives of Ru<sub>3</sub>(CO)<sub>12</sub>; similar reagents have been prepared using PPh<sub>2</sub>Me as structural and spectral models, Table I.<sup>6,7</sup> The (EtO)<sub>3</sub>Si— functionality allows the covalent attachment of the Ru species to the SiO<sub>2</sub> surface. We use [S]—LRu(CO)<sub>4</sub> and [S]—L<sub>3</sub>Ru<sub>3</sub>(CO)<sub>9</sub> to represent the two systems. Infrared and uv-vis spectra Table I, and elemental analyses clearly establish that metal carbonyl moieties can be confined to SiO<sub>2</sub>. There is a rather significant change in the relative intensities of the infrared features upon reaction to anchor Ru(CO)<sub>4</sub>L and Ru<sub>3</sub>(CO)<sub>9</sub>L<sub>3</sub> to the surface. Metal carbonyl absorptions in the CO stretching region are very sensitive to local structure. The uv-vis spectra of the [S]—LRu(CO)<sub>4</sub> and [S]—L<sub>3</sub>Ru<sub>3</sub>(CO)<sub>9</sub> accord well with solution absorption spectra of Ru(CO)<sub>4</sub>L and Ru<sub>3</sub>(CO)<sub>9</sub>L<sub>3</sub>, Table I. From elemental analyses the key elements, Ru and P, are present in a ratio, ~1/1, that is consistent with the retention of the species claimed.<sup>10</sup> From the analyses the coverage ( $1.3 \times 10^{-11}$  mol/cm<sup>2</sup>) is less than what would be regarded as a monolayer ( $\sim 10^{-10}$  mol/cm<sup>2</sup>), assuming that the coverage is uniform. Since the anchoring group is (EtO)<sub>3</sub>Si—, the Ru species may be anchored to the surface in polymeric amounts,<sup>8</sup> but the low coverage tends to rule out extensive polymerization. We shall assume that the coverage is uniform and that extensive polymerization does not occur. Photochemical results described below are consistent with this assumption.

Paralleling results reported earlier for Ru(CO)<sub>4</sub>PPh<sub>3</sub> and Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub>,<sup>1b</sup> the photochemistry of [(EtO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>]Ru(CO)<sub>4</sub> and [(EtO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>]<sub>3</sub>Ru<sub>3</sub>(CO)<sub>9</sub> is represented by equations (5)-(7).<sup>11</sup>

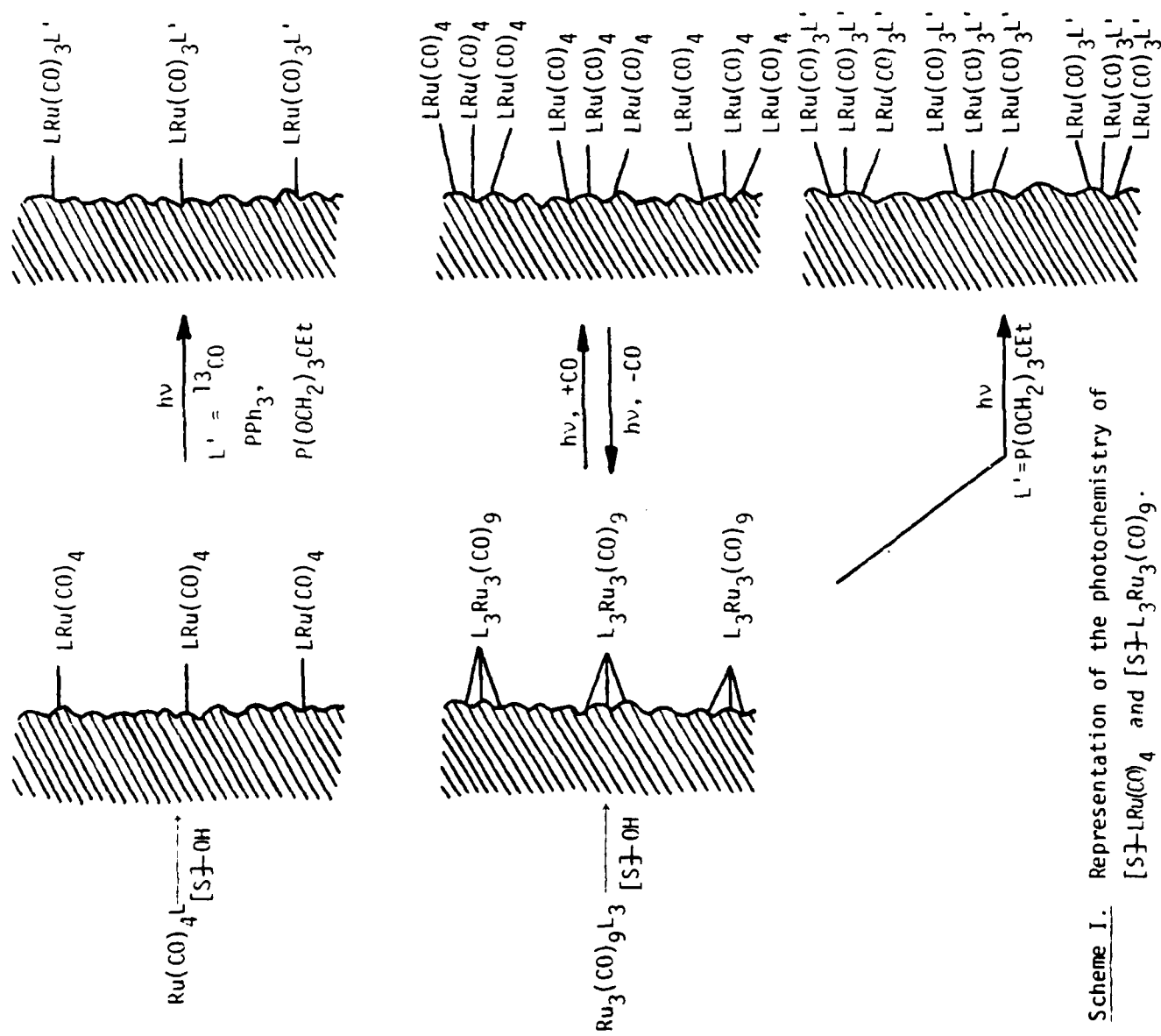






The results are consistent with dissociative loss of CO from the  $\text{Ru}(\text{CO})_4\text{L}$  ( $\text{L} = \text{PPh}_3, \text{PPh}_2\text{R}$  ( $\text{R} = \text{alkyl}$ )) species; the quantum yield at 366 nm is  $0.40 \pm 0.05$  for reaction according to (5) for  $\text{L}' = \text{PPh}_3, \text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$  at 0.1 M in degassed toluene solution at 25°C. The photoreaction of  $\text{Ru}_3(\text{CO})_9\text{L}_3$  is consistent with Ru-Ru bond cleavage as the prompt result of excited state decay. The quantum yield for the reaction represented by equation (7) at an  $\text{L}'$  concentration of 0.1 M in toluene is  $\sim 10^{-3}$  for 436 nm excitation. Fortunately, the  $\text{Ru}_3(\text{CO})_9\text{L}_3$  species absorb at lower energy ( $\lambda_{\text{max}} \approx 490 \text{ nm}$ ,  $\epsilon = 14,000$ ) than do the  $\text{Ru}(\text{CO})_4\text{L}$  species ( $\lambda_{\text{max}} \approx 260 \text{ nm}$ ,  $\epsilon = 9000$ ) allowing completely selective excitation of the  $\text{Ru}_3(\text{CO})_9\text{L}_3$  in the presence of large concentrations of  $\text{Ru}(\text{CO})_4\text{L}$ .

Irradiation of  $[\text{S}]-\text{LRu}(\text{CO})_4$  and  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  suspended in degassed isooctane solutions results in chemical changes consistent with dissociative loss of CO from the mononuclear species and metal-metal bond cleavage of the trinuclear species. Scheme I summarizes the chemistry that has been done. Irradiation of  $[\text{S}]-\text{LRu}(\text{CO})_4$  suspended in degassed isooctane containing 0.05 M  $\text{PPh}_3$  or  $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$  gives infrared spectral changes consistent with the formation of  $[\text{S}]-\text{LRu}(\text{CO})_3\text{L}'$ , where L and L' are trans, axial ligands as in the  $\text{Ru}(\text{CO})_3\text{LL}'$  complexes, Table I, since there is only one infrared absorption in the CO stretching region. The key fact is that the spectral changes accompanying the irradiation of  $[\text{S}]-\text{LRu}(\text{CO})_4$  in the presence of L' reveal a single CO stretch at a position very close to that for  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]\text{Ru}(\text{CO})_3\text{L}'$  formed photochemically. The conversion is clean and gives a good yield of the  $[\text{S}]-\text{LRu}(\text{CO})_3\text{L}'$  based on the relative absorptivities of  $\text{Ru}(\text{CO})_4\text{L}$  and  $\text{Ru}(\text{CO})_3\text{LL}'$ . The irradiation of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  in the presence of  $\text{L}' =$



Scheme I. Representation of the photochemistry of  $[\text{S}]-\text{LRu(CO)}_4$  and  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$ .

$\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$  yields an infrared spectral change to give a single CO stretch in exactly the same position as for  $[\text{S}]-\text{LRu}(\text{CO})_3\text{L}'$  formed by irradiation of  $[\text{S}]-\text{LRu}(\text{CO})_4$ . Thus, the surface-confined cluster appears to undergo metal-metal bond cleavage upon photoexcitation, paralleling the solution analogue.

An important finding relates to the photochemistry of the  $[\text{S}]-\text{LRu}(\text{CO})_4$  formed from irradiation of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  under CO. As illustrated in Figure 1, 436 nm irradiation of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  under 1 atm CO yields a spectrum identical to that for  $[\text{S}]-\text{LRu}(\text{CO})_4$  synthesized according to equation (4). The key finding is that 355 nm irradiation of the photogenerated  $[\text{S}]-\text{LRu}(\text{CO})_4$  while purging out CO leads to the nearly quantitative regeneration of the  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$ . In sharp contrast, 355 nm irradiation of  $[\text{S}]-\text{LRu}(\text{CO})_4$  formed by the procedure in equation (4) yields loss of all metal carbonyl absorptions under the same conditions, and we find no evidence for the formation of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$ . The difference, as illustrated in Scheme I, is that  $[\text{S}]-\text{LRu}(\text{CO})_4$  from synthesis by equation (4) yields  $-\text{Ru}(\text{CO})_4$  centers that are statistically far apart from each other compared to the  $-\text{Ru}(\text{CO})_4$  center from the 436 nm irradiation of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  under CO. The nearly quantitative photochemical disassembly-reassembly of the  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  system establishes several important facts: (1) the  $-\text{Ru}(\text{CO})_4$  centers formed photochemically are immobile, remaining close enough to each other to reform the original cluster by photochemical extrusion of CO; (2) each Ru of the  $\text{Ru}_3$  species is anchored to the surface via the  $\text{>SiCH}_2\text{CH}_2\text{PPh}_2$  ligand, otherwise the recovery of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  would be poor; and (3) the  $-\text{Ru}(\text{CO})_4$  centers attached according to equation (4) are sufficiently isolated to prevent cluster formation even though CO is ejected photochemically (Figure 1); thus, photogenerated 16-valence-electron  $[\text{S}]-\text{LRu}(\text{CO})_3$  species can be persistently isolated from each other when the coverage is dilute. In no case do we find photochemical extrusion of Ru carbonyl species into the hydrocarbon solution; the Ru-P

bond is photochemically inert, as reported earlier for  $\text{Ru}(\text{CO})_4\text{PPh}_3$  and related complexes.<sup>1b</sup>

The photochemistry of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  departs from that of its solution analogue in that irradiation in the presence of  $\text{L}' = \text{PPh}_3$  fails to produce  $[\text{S}]-\text{LRu}(\text{CO})_3\text{L}'$  as would be expected based on the ability to photochemically form  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]\text{Ru}(\text{CO})_3\text{L}'$  from the trinuclear species. However, irradiation of  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  in the presence of  $\text{L}' = \text{CO}$  or  $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$  rapidly and cleanly yields  $[\text{S}]-\text{LRu}(\text{CO})_3\text{L}'$ . The conclusion is that the closely spaced, immobilized Ru atoms in  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  are much more structurally demanding precluding reaction with a large ligand such as  $\text{PPh}_3$  (cone angle =  $145^\circ$ )<sup>11</sup> whereas a small ligand like  $\text{CO}$ , or  $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$  (cone angle  $\approx 100^\circ$ )<sup>12</sup> can yield mononuclear products. Preliminary studies show that  $[\text{S}]-\text{LRu}(\text{CO})_4$  and  $[\text{S}]-\text{L}_3\text{Ru}_3(\text{CO})_9$  each yield different distributions of alkene photocatalysis products under isomerization<sup>1b</sup> or hydrosilation conditions<sup>1c</sup> compared to their solution analogues, consistent with different structural demands at the photogenerated sites. These results will be reported subsequently.

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9. High surface area  $\text{SiO}_2$  (400  $\text{m}^2/\text{g}$ ) purchased from Alfa was pretreated by heating at  $\sim 250^\circ\text{C}$  under vacuum ( $10^{-2}$  torr) for 48 h. A typical preparation of  $[\text{S}]\text{-LRu}(\text{CO})_4$  (yellow) or  $[\text{S}]\text{-L}_3\text{Ru}_3(\text{CO})_9$  (red) involves the suspension of  $\sim 1$  g of pretreated  $\text{SiO}_2$  in toluene. Excess  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]\text{Ru}(\text{CO})_4$  or  $[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]_3\text{Ru}_3(\text{CO})_9$  is added and the suspension stirred at  $25^\circ\text{C}$  for 24 h under  $\text{N}_2$ . The solid is collected by filtration and washed repeatedly with toluene, dried under vacuum and stored under  $\text{N}_2$ . Control experiments using  $\text{Ru}(\text{CO})_4\text{PPh}_2\text{Me}$  or  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{Me})_3$  as the derivatizing reagents yield no surface-confined metal carbonyls yielding only white, underivatized  $\text{SiO}_2$  after washing with toluene.
10. The elemental analysis of  $[\text{S}]\text{-LRu}(\text{CO})_4$  is 1.57% Ru and 0.39% P (%'s are %'s by weight) giving an atom ratio Ru/P close to the expected 1/1. The

coverage is thus  $3.9 \times 10^{-11}$  mol/cm<sup>2</sup>, assuming the surface area to be 400 m<sup>2</sup>/g. The elemental analysis of  $[\text{S}]\text{-L}_3\text{Ru}_3(\text{CO})_9$  is 3.29% Ru and 0.95% P, again giving a Ru/P atom ratio close to the expected 1/1 and a coverage of  $2.7 \times 10^{-11}$  mol/cm<sup>2</sup>. Elemental analyses were performed by Galbraith Laboratories.

11. Irradiations were carried out using a GE Black Lite for 355 nm + 20 nm or a Hanovia 450 W medium pressure Hg lamp with Corning glass filters, to isolate the 366 or 436 nm emission.
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Table I. Spectroscopic Data for Relevant Compounds.<sup>a</sup>

Compound	ir $\nu_{\text{CO}}$ , $\text{cm}^{-1}$ ( $\epsilon$ or relative o.d.)	uv-vis $\lambda_{\text{max}}$ , nm ( $\epsilon$ )	
$\text{Ru}(\text{CO})_4(\text{PPh}_2\text{Me})$	2060(2710), 1984(1810), 1946(4860)	254(9150) <sup>b</sup>	(absorption)
$[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]_2\text{Ru}(\text{CO})_4$	2058(2800), 1982(1350), 1946(4840)	257(9190) <sup>b</sup>	(absorption)
$[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]_2\text{Ru}(\text{CO})_3\text{PPh}_3$	1896(5040)	---	---
$[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]_2\text{Ru}(\text{CO})_3(\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3)$	1917(—)	---	---
$[\text{S}]\text{-LRu}(\text{CO})_4$ <sup>c</sup>	2059(1.0), 1995(1.0), 1952(0.6)	255	(photoacoustic)
$[\text{S}]\text{-LRu}(\text{CO})_3(\text{PPh}_3)$	1900(1.0)	---	---
$[\text{S}]\text{-LRu}(\text{CO})_3(\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3)$ <sup>d</sup>	1920(1.0)	---	---
$\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{Me})_3$	2042(320), 1970(2800), 1943(1510)	484(13600), 364(sh)	(absorption)
$[(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{PPh}_2]_3\text{Ru}_3(\text{CO})_9$	2044(240), 1970(2790), 1940(850)	488(13200), 366(sh)	(absorption)
$[\text{S}]\text{-L}_3\text{Ru}_3(\text{CO})_9$	2056(0.8), 1988(1.0), 1950(sh), 2066(0.8) <sup>e</sup> , 2004(1.0) <sup>e</sup> , 1965(sh) <sup>e</sup>	490, 370(sh)	(photoacoustic)

<sup>a</sup>All measurements were made in toluene solution at 25°C for soluble Ru complexes using conventional techniques.

For the surface-confined species infrared spectra were typically recorded as Nujol mulls by Fourier transform infrared (Nicolet 7199) and uv-visible absorption data were obtained using a Cary 17 for soluble species and photoacoustic spectra were obtained using a PAR 6001 PAS spectrometer for powders.

<sup>b</sup>Measured in hexane solution at 25°C.

<sup>c</sup>Prepared via equation (4) or from irradiation of  $[\text{S}]\text{-L}_3\text{Ru}_3(\text{CO})_9$  under CO.

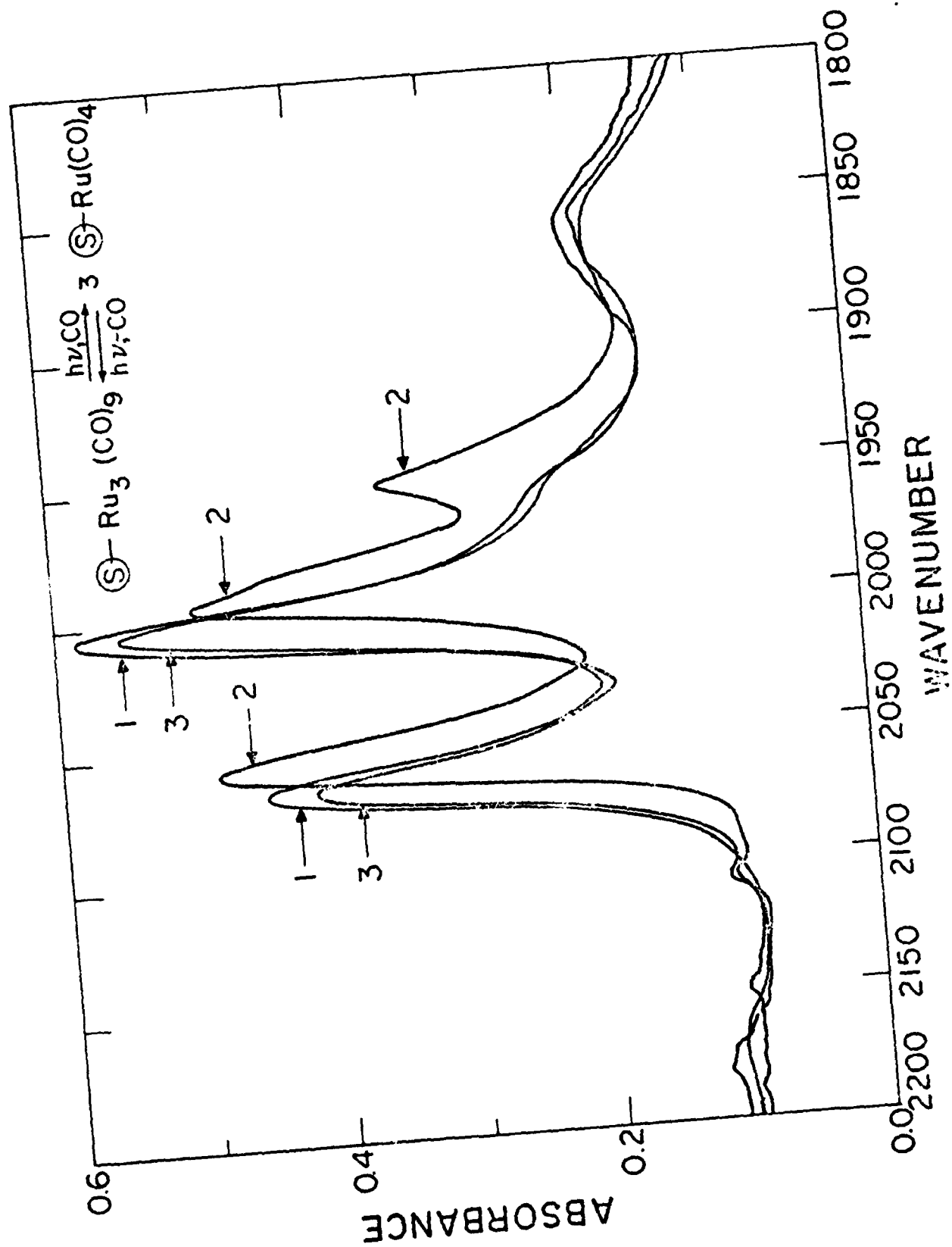
<sup>d</sup>Generated from either  $[\text{S}]\text{-LRu}(\text{CO})_4$  or  $[\text{S}]\text{-L}_3\text{Ru}_3(\text{CO})_9$  irradiated in the presence of  $\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3$ .

<sup>e</sup>Measured in a KBr pellet.

Figure Caption

Figure 1. Representation of infrared spectral changes associated with the 436 nm irradiation of  $[S]-L_3Ru_3(CO)_9$  (1) under 1 atm CO, suspended in isooctane to yield  $[S]-LRu(CO)_4$  (2). The irradiation of the photogenerated  $[S]-LRu(CO)_4$  for 10 h with  $355\text{ nm} \pm 20\text{ nm}$  light while purging the isooctane suspension with  $N_2$  leads to the nearly quantitative regeneration of  $[S]-L_3Ru_3(CO)_9$ , spectrum (3). Spectra are for  $[S]-LRu(CO)_4/[S]-L_3Ru_3(CO)_9$  in KBr pellets typically prepared by intimate mixing of 0.01 g of the powder with 3.0 g of KBr. Pellets of ~0.4 g are pressed at 20,000 psi to give 1.0 cm diameter, ~0.4 mm thick disks.





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